

# Fewest-switches with time uncertainty: A modified trajectory surface-hopping algorithm with better accuracy for classically forbidden electronic transitions

Ahren W. Jasper, Samuel N. Stechmann, and Donald G. Truhlar<sup>a)</sup>

*Department of Chemistry and Supercomputer Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431*

(Received 6 December 2001; accepted 4 January 2002)

We present a modification of Tully's fewest-switches (TFS) trajectory surface-hopping algorithm (also called molecular dynamics with quantum transitions) that is called the fewest-switches with time uncertainty (FSTU) method. The FSTU method improves the self-consistency of the fewest-switches algorithm by incorporating quantum uncertainty into the hopping times of classically forbidden hops. This uncertainty allows an electronic transition that is classically forbidden at some geometry to occur by hopping at a nearby classically allowed geometry if an allowed hopping point is reachable within the Heisenberg interval of time uncertainty. The increased accuracy of the FSTU method is verified using a challenging set of three-body, two-state test cases for which accurate quantum-mechanical results are available. The FSTU method is shown to be more accurate than the TFS method in predicting total nonadiabatic quenching probabilities and product branching ratios. © 2002 American Institute of Physics. [DOI: 10.1063/1.1453404]

## I. INTRODUCTION

Semiclassical trajectory simulations<sup>1–11</sup> have proven useful for modeling electronically nonadiabatic dynamics for a wide variety of chemical systems,<sup>11–23</sup> and we have recently engaged in a systematic set of studies designed to test and improve these methods.<sup>11–23</sup> Semiclassical trajectory methods are especially interesting because they are readily applicable to large systems (e.g., bacteriorhodopsin) for which a full quantum dynamical treatment is likely to remain prohibitively computationally expensive for some time. Before applying semiclassical methods to large systems, it is advisable to validate them by studying smaller systems where benchmarks are available or can be calculated. Fortunately, the increased availability of converged quantum-mechanical calculations for fully three-dimensional atom-diatom systems<sup>12–14,16–19,23,24</sup> has provided a useful set of benchmark test cases for judging the accuracy of several semiclassical trajectory methods<sup>11–14,16,17,19–23,25–31</sup> that have been proposed. The set of test cases, if carefully designed, also provides a means of systematically improving the semiclassical trajectory approach by identifying the dominant errors and developing methods that reduce these errors.

Although many of the existing and newly designed semiclassical trajectory methods show promise, the fewest-switches<sup>8,27,32</sup> surface-hopping<sup>1,2,5,6,8,9,11,12,14,16–18,23,26,27,30–41</sup> algorithm of Tully (called here TFS and elsewhere molecular dynamics with quantum transitions, or MDQT) has proved to be surprisingly robust despite its simple formulation.<sup>11–14,16–23</sup> Trajectory surface-hopping methods assume that the nuclear dynamics of the system may be approximately described by an ensemble of noninteracting tra-

jectories, and that each trajectory evolves classically under the influence of a potential energy surface that corresponds locally to a single electronic state. Electronic transitions are incorporated into the classical nuclear dynamics by interrupting the single electronic surface propagation with a series of hopping decisions. At a hopping decision, a surface switch (or hop) from the occupied electronic state  $i$  to some target electronic state  $j$  occurs with a probability  $P_h^{ij}$ , where  $P_h^{ij}$  is usually some function of the quantum-mechanical electronic state probability density integrated along the classical trajectory. The TFS algorithm defines  $P_h^{ij}$  such that hopping is minimized in the sense that trajectories hop only when there is a net flow of electronic state probability density out of the occupied state during the time interval between hopping decisions. In general, the target state and the occupied state may have different potential energies at a surface hop, and when a trajectory hops successfully the nuclear momentum is adjusted along some hopping vector  $\mathbf{h}$  (usually the nonadiabatic coupling vector<sup>1,8</sup>) such that total energy is conserved.

As mentioned above, the TFS method has been applied with success to a wide variety of chemical systems. However, some limitations and ambiguities in the TFS method (and surface-hopping methods in general) were pointed out in the original formulation<sup>27</sup> and have also been discussed more recently.<sup>23,31,41</sup> Here, we focus attention on the problem of frustrated hopping.<sup>16–18,23,30,31,41–44</sup> The TFS algorithm may give a nonzero value of  $P_h^{ij}$  (and therefore may call for a surface hop) at a geometry along the trajectory where the energy gap between the occupied and the target electronic state is greater than the maximum classically allowed nuclear energy adjustment that is achievable by adjusting the momentum in the direction of  $\mathbf{h}$ , i.e., a hop may be called for when the nuclear momentum cannot be adjusted along  $\mathbf{h}$

<sup>a)</sup>Electronic mail: truhlar@umn.edu

such that total energy is conserved. Hopping attempts of this type are said to be “classically forbidden” or “frustrated.” The presence of frustrated hopping ruins the self-consistency built into the TFS method and can therefore lead to an incorrect final electronic state distribution of trajectories.

Recently, we have systematically tested<sup>23</sup> several variants of the TFS method that have been proposed to deal with the problem of frustrated hopping. Unfortunately, none of the methods tested was completely satisfactory. In general, we found that the loss of self-consistency that results from frustrated hopping causes the TFS method to significantly overestimate the total probability of nonadiabatic quenching for weakly coupled systems. Conversely, by artificially allowing *all* trajectories that experience classically forbidden hopping attempts to switch electronic surfaces (simulating a fully self-consistent result), the total probability of nonadiabatic quenching is significantly underestimated. This numerical result motivates the search for a modification of the TFS method that allows some but not all hops that are frustrated to somehow switch electronic states, and in the present paper we describe such a method.

One can identify two limitations of the TFS semiclassical trajectory approach that lead to frustrated hopping: (1) The TFS semiclassical trajectory approach algorithm does not allow tunneling into a new electronic state, and (2) the TFS hopping probability does not properly treat electronic state decoherence (also called dephasing). The first consideration (1) is a consequence of the classical trajectory approach. The quantum-mechanical nuclear wave function of a dynamical system may have a finite probability amplitude in a region where classical trajectories are forbidden by energy conservation. These quantum-mechanical “tails” may induce physically meaningful electronic transitions in regions where surface hops are classically energetically forbidden, and this is a manifestation of tunneling. Within the classical trajectory approach these meaningful electronic state tunneling transitions result in frustrated hops. The second consideration (2) is a result of the formulation of the TFS hopping probability. Specifically, the TFS method gives the fully self-consistent electronic state populations at all times only for systems with degenerate electronic states, i.e., only when the ensembles of trajectories that occupy different electronic states do not separate in phase space. Of course, realistic chemical systems feature nondegenerate electronic states, often with greatly disparate potential energy topographies. Nondegenerate potential energy surfaces lead to decoherent ensembles of trajectories in each electronic state,<sup>20,21,45</sup> and this decoherence results in a decreased probability of electronic transition. The TFS formulation does not properly treat electronic state decoherence, and therefore the TFS method overpredicts electronic transitions, especially in classically forbidden regions where classical trajectories cannot exist in the target electronic state.

The frustrated hops associated with (1) above are considered physically meaningful in the fewest-switches surface-hopping context and should be allowed to switch electronic states. The frustrated hops resulting from (2) above are not physically meaningful and should be ignored. These two considerations provide a reasonable means of in-

terpreting the numerical result obtained in our previous study<sup>23</sup> that was discussed above. The present paper describes a modification of the TFS algorithm that first identifies if a frustrated hop is physically meaningful and is a result of electronic state tunneling [consideration (1)] or if a frustrated hop is not physically meaningful and is a result of the improper treatment of electronic state decoherence [consideration (2)]. The method then allows trajectories that experience physically meaningful frustrated hops to tunnel to a nearby classically allowed geometry and switch electronic states. The new semiclassical trajectory method is called the fewest-switches with time uncertainty (FSTU) method and is identical to the TFS method for classically allowed surface hops.

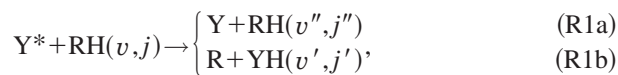
We tested the FSTU method against the TFS method on a family of weakly coupled systems<sup>23</sup> that was designed to be very sensitive to the treatment of classically forbidden hops. The results of these tests show that the nonlocal hopping (as in the FSTU method) is necessary for properly modeling electronic transitions and accurately predicting the total nonadiabatic quenching probability and the product branching ratio.

The modification of the TFS method proposed here is similar in its aims to a recent attempt to modify the surface-hopping method that was proposed by Zhu *et al.*,<sup>43,44</sup> although we each arrived at our starting point and our modifications independently by separate routes. Both methods remove frustrated hopping by allowing nonlocal surface hops; the two methods will be compared in more detail in Sec. V.

This paper is organized as follows: Section II summarizes the important features of the model surfaces. The semiclassical calculations, including the details of the FSTU method, are described in Sec. III, and the results are presented in Sec. IV. The results are discussed and summarized in Secs. V and VI, respectively.

## II. MODEL POTENTIAL ENERGY MATRICES

The YRH family<sup>23</sup> of three-body potential energy matrices (PEMs) used to test the FSTU method models the nonadiabatic scattering process of an electronically excited model Y atom and a diatomic molecule RH:



where the asterisk indicates electronic excitation, and the primes on the vibrational  $v$  and rotational  $j$  quantum numbers indicate that these quantities are not necessarily conserved. The mass combination for the model atoms was chosen to be 10 and 6 amu for the Y and R atoms, respectively. The H atom has the mass of hydrogen, i.e., 1.007 83 amu. Details of the family of YRH surfaces are presented in an earlier work.<sup>23</sup> Briefly, the family of YRH surfaces is made up of four members, and each member differs from the others only in the magnitude of the diabatic coupling. The maximum diabatic coupling for the four potential matrices discussed in the present work are  $U_{12}^{\max} = 0.20, 0.10, 0.03$ , and 0.01 eV.

As discussed below, the semiclassical trajectory calculations were carried out in the adiabatic representation. The adiabatic potential energy surfaces were obtained by diagonalizing the diabatic PEM. The adiabatic surfaces are coupled by the scalar product of the velocity and the nonadiabatic coupling vector  $\mathbf{d}$ .<sup>1,8</sup> As discussed elsewhere,<sup>18</sup> one can calculate  $\mathbf{d}$  without approximation from the diabatic matrix elements and their gradients.

The initial scattering conditions will be labeled by the shorthand  $(E/\text{eV}, j)$  where  $E/\text{eV}$  is the total energy in eV, and  $j$  is the initial rotational quantum number of the RH diatom. The initial vibrational quantum number of the RH diatom is zero, and the total angular momentum is also zero. We consider a total of 12 test cases; for each of the four PEMs discussed above, we consider three sets of initial conditions: (1.10, 0); (1.10, 6); and (1.02, 0).

### III. SEMICLASSICAL TRAJECTORY CALCULATIONS AND TIME-UNCERTAINTY SWITCHING ALGORITHM

Semiclassical trajectory surface-hopping calculations were carried out using version 6.6 of the NAT computer code.<sup>46</sup> Details of our implementation of the semiclassical trajectory algorithm including the selection of the initial conditions, the propagation of the classical trajectories, the implementation of the fewest-switches algorithm, and the final-state analysis may be found elsewhere.<sup>2,14,23</sup> Briefly, all of the calculations reported here were carried out in the adiabatic representation, and the hopping vector  $\mathbf{h}$  was taken to be a unit vector in the direction of the nonadiabatic coupling vector  $\mathbf{d}$ .<sup>1,8</sup> This choice for  $\mathbf{h}$  has been justified theoretically<sup>34,37,47</sup> and numerically.<sup>12,14</sup>

The fewest-switches with time uncertainty (FSTU) method is a modification of the TFS method that incorporates nonlocal hopping such that some (but not all) frustrated hops are allowed to switch electronic states. The FSTU method is identical to the TFS method except when a trajectory experiences a frustrated hop. Specifically, the quantum-mechanical electronic state population density  $P_i(t)$  is obtained by integrating the solution of the time-dependent Schrödinger equation along the classical trajectory  $\mathbf{R}(t)$ , and is given by (in the adiabatic representation for a two-state system)<sup>1,8,27</sup>

$$\dot{P}_i(t) = -2 \operatorname{Re}[a_{ij}^*(t)\dot{\mathbf{R}}(t) \cdot \mathbf{d}], \quad (1)$$

where the overdot indicates a time derivative,  $i \neq j$ ,  $a_{ij}$  is the cross term of the electronic state density matrix (e.g.,  $P_i = a_{ii}$ ),  $\dot{\mathbf{R}}$  is the velocity of the classical trajectory,  $\mathbf{d}$  is the nonadiabatic coupling vector between states  $i$  and  $j$ , and  $i = 1$  for the ground electronic state and  $i = 2$  for the excited electronic state. The fewest-switches<sup>8,27</sup> hopping probability  $P_h^{ij}$  is computed from  $P_i(t)$

$$P_h^{ij}(t) = \max\left(0, \frac{-\dot{P}_i(t)\delta t}{P_i(t)}\right), \quad (2)$$

where the system is currently occupying state  $i$ , and  $\delta t$  is the time interval between hopping decisions. If the fraction of trajectories in each electronic state  $F_i(t)$  is equal to the

quantum-mechanical electronic state density  $P_i(t)$  (for all  $i$ ) at the start of the simulation, trajectories switch surfaces according to Eq. (2), and *all* surface hops are allowed, then  $F_i(t)$  and  $P_i(t)$  will be equal for all  $t$ . [Of course,  $F_i(t)$  and  $P_i(t)$  will not be *exactly* equal due to the finite number of trajectories in the computational ensemble.] If a surface hop is called for by Eq. (2) and the hop is frustrated, this self-consistency will no longer be maintained. We note that the presence of frustrated hops results in a “fewer-than-fewest-switches” method, and we will comment on this at the end of Sec. V.

The FSTU treatment of a frustrated hop is discussed next. The time-energy version of the uncertainty principle<sup>48</sup>

$$\Delta E \Delta t \approx \hbar, \quad (3)$$

may be interpreted as the system borrowing some energy  $\Delta E$  for some time  $\Delta t$ . We incorporate this feature in the semiclassical theory by allowing a trajectory  $\mathbf{R}(t)$  that experiences a frustrated hop to tunnel and hop successfully at some nearby geometry along  $\mathbf{R}(t)$  that it is classically allowed and where the time that the trajectory tunnels is within the time interval  $\Delta t$  given by Eq. (3). Specifically, if a hop at time  $t_0$  is classically forbidden, the trajectory is assumed to hop at some time  $t_h$  (if any such time exists) that minimizes  $|t_0 - t_h|$  subject to the following two criteria: (1) a hop is classically allowed at  $\mathbf{R}(t_h)$ , and (2) the difference between  $t_0$  and  $t_h$  satisfies

$$|t_0 - t_h| \leq \hbar/2\Delta E, \quad (4)$$

where the factor of  $\frac{1}{2}$  introduced into Eq. (4) ensures that the distribution of nonlocal hops around  $t_0$  will have a maximum width of  $\Delta t$  given by Eq. (3). In Eq. (4),  $\Delta E$  is the difference between the potential energy gap at  $\mathbf{R}(t_0)$  and the available kinetic energy along the hopping vector at time  $t_0$ , i.e.,  $\Delta E$  is the energy that the trajectory would need to “borrow” in order to hop at  $t_0$ . Notice that the trajectory may hop nonlocally both forward and backward in time. For some frustrated hops these criteria cannot be satisfied, and these frustrated hops are thought to be caused by the improper treatment of decoherence effects (as discussed in Secs. I and V) and are ignored.

Our development of the FSTU method is a culmination of a series of studies<sup>11–23</sup> in which we have systematically examined and tested several possible options and variations in the surface-hopping approach. This includes comparing the original fewest-switches criterion for invoking a surface-hopping decision to the Blais–Truhlar<sup>12–16,26</sup> and generalized Blais–Truhlar<sup>16</sup> criteria, comparing diabatic and adiabatic representations for the electronic probability amplitude and trajectory propagation,<sup>11,18–22</sup> testing the effect of symmetrizing the speed or coupling in computing the hopping probability,<sup>11,23</sup> comparing various choices for the hopping vector,<sup>13,15,17</sup> testing the effect of rotating the hopping vector when the momentum component along the hopping vector is too small to allow a hop,<sup>11,17,18,23</sup> testing various combinations of reflecting or ignoring hops when they are frustrated,<sup>23</sup> comparing energy-conserving to energy-nonconserving methods for assigning final discrete quantum numbers on the basis of the continuous final trajectory



TABLE I. Mean unsigned relative errors (MUREs) for the TFS and FSTU methods averaged over 12 test cases.

Method	$P_R$	$\langle v' \rangle$	$\langle j' \rangle$	$P_Q$	$\langle v'' \rangle$	$\langle j'' \rangle$	$F_R$	$P_N$	Prob. <sup>a</sup>	Mom. <sup>b</sup>	All <sup>c</sup>
TFS <sup>d</sup>	1.36	0.12	0.14	0.29	0.23	0.67	0.32	0.93	0.73	0.29	0.51
FSTU	0.73	0.17	0.14	0.19	0.38	0.91	0.16	0.67	0.44	0.40	0.42

<sup>a</sup>Average MURE for the probabilities  $P_R$ ,  $P_Q$ ,  $F_R$ , and  $P_N$ .<sup>b</sup>Average MURE for the moments  $\langle v' \rangle$ ,  $\langle j' \rangle$ ,  $\langle v'' \rangle$ , and  $\langle j'' \rangle$ .<sup>c</sup>Average MURE for all eight observables.<sup>d</sup>The MUREs for the TFS method were computed from the TFS-(+,+) data in Ref. 23.

variables,<sup>11,14,16,23</sup> and comparing histogram methods to smooth sampling for assigning final discrete quantum numbers.<sup>11,14,16,17,23</sup> Consideration of what we learned in those studies<sup>11–23</sup> and from related work<sup>30,49,50</sup> not only motivated the present suggestion of an improved fewest-switches algorithm but also—very significantly—gives us confidence that the improved performance (see below) of the FSTU scheme is not simply the result of an unphysical cancellation of errors resulting from poor methodological decisions for the other aspects of the surface-hopping scheme. Our final recommendations for the best way to carry out surface-hopping calculations can be summarized as follows: (1) Choose hopping decision locations on the basis of the fewest-switches with time uncertainty algorithm. (2) Choose the electronic state representation (adiabatic or diabatic) by the Calaveras County<sup>11</sup> criterion. (3) Do not employ symmetrization schemes. (4) Choose the hopping vector along the nonadiabatic coupling vector without rotation. (5) If hops are frustrated, ignore them. (6) Assign electronic states according to the surface on which a trajectory finishes, and assign final vibrational and rotational quantum numbers by either the energy nonconserving histogram (ENH) method,<sup>14,16,17</sup> which gives a well defined error estimate,<sup>2</sup> or the energy nonconserving quadratic smooth sampling (ENQSS) method,<sup>14,17,49</sup> which may be significantly more accurate or give better statistics (but without a well-defined error estimate), with the possibility in reserve that a more sophisticated final-state algorithm may be needed when one is near an energy threshold for a final state of interest. The combination of all these choices defines the standard FSTU algorithm. In the present paper, all reported results were obtained by the ENH scheme, but the ENQSS results are very similar.

All calculations in the present paper were carried out using the adaptive integration algorithm that we designed for fewest-switches surface-hopping calculations in a previous paper.<sup>17</sup> This algorithm uses a Bulirsch–Stoer integrator with polynomial extrapolation,<sup>12,51</sup> and is specifically modified to prohibit the integrator from stepping over peaks and local minima in the electronic probabilities.<sup>17</sup> For the present calculations the parameters<sup>17</sup> were given the following values:  $\varepsilon_{BS} = 10^{-12} E_h$  ( $1 E_h = 27.211$  eV) and  $h_{min} = 10^{-4}$  a.u. ( $1$  a.u. =  $2.4189 \times 10^{-2}$  fs), which gives convergence for the TFS results. For the FSTU results, another consideration arises. In particular, we found that in typical cases  $\hbar/2\Delta E$  is only a few times larger than the step size required to converge the integration of the coupled differential equations. Thus, one may require a smaller step size for the integration to the final value of  $t_h$  than for the rest of the propagation. In the present application we selected  $t_h$  from a set of discrete

times obtained by integrating the classical trajectories numerically, and we checked that the FSTU results are well converged with respect to step size.

#### IV. RESULTS

We tested the FSTU method on the four YRH systems using the three sets of initial conditions described in Sec. II, for a total of 12 test cases. Table I shows the mean unsigned relative error (MURE) of the vibrational  $v$  and rotational  $j$  moments for the reactive (single primes) and nonreactive electronically quenched (double primes) products, the probability of reaction  $P_R$ , the probability of nonreactive electronic quenching  $P_Q$ , the total nonadiabatic quenching probability  $P_N = P_R + P_Q$ , and the product branching ratio  $F_R = P_R/P_N$ , obtained by averaging the unsigned relative errors (UREs) for the 12 test cases. Also shown is the MURE for the TFS method. The TFS semiclassical trajectory results and the fully converged quantum-mechanical results used to compute the UREs were taken from Ref. 23. Note that of the several variants of the TFS method discussed in Ref. 23, we used the data for the TFS variant where all frustrated hopping attempts were ignored [called TFS-(+,+) in Ref. 23]. Table I shows that nonlocal hopping (as in the FSTU method) reduces the error in the reaction probability by a factor of 1.9, the error in the quenching probability by a factor of 1.5, the error in the product branching ratio by a factor of 1.4, and the error in the total nonadiabatic probability by a factor of 2, where all errors are MUREs. The MUREs in the reactive moments are similar for the FSTU and TFS methods, whereas the FSTU method is less accurate by a factor of 1.5 for the quenching moments.

Table II shows the UREs for the total nonadiabatic probability  $P_N$  and the product branching ratio  $F_R$  for each of the 12 test cases. For  $P_N$ , the FSTU method is less accurate than the TFS method for only two of the 12 test cases, and in these two cases both the FSTU and the TFS method have small UREs. For the other ten test cases, the FSTU method is more accurate than the TFS method for  $P_N$ ; the URE for the FSTU method is smaller than the URE for the TFS method by a factor of  $\sim 2$  for six cases, a factor of  $\sim 4$  for two cases, and factors of 5.8 and 9.3 for the remaining two cases. For the product branching ratio  $F_R$ , the FSTU method is slightly less accurate than the TFS method for four of the 12 cases (by an average factor in the UREs of 1.1). For the remaining eight cases, the FSTU method is more accurate than the TFS method in predicting  $F_R$ ; the URE in  $F_R$  is smaller for the FSTU method by factors of 1.4–2.0 for six cases, and factors of 3.0 and 4.9 for the remaining two cases.

TABLE II. Unsigned relative errors (UREs) for the TFS and FSTU methods for the 12 test cases.

I. C. <sup>a</sup>	$U_{12}^{\max}/\text{eV}$	$P_N$		$F_R$	
		TFS	FSTU	TFS	FSTU
(1.10, 0)	0.20	0.75	0.31	0.64	0.33
	0.10	0.18	0.05	0.48	0.28
	0.03	0.49	0.08	0.31	0.10
	0.01	0.43	0.24	0.14	0.15
(1.10, 6)	0.20	0.15	0.06	0.47	0.33
	0.10	0.41	0.26	0.61	0.66
	0.03	0.05	0.10	0.39	0.49
	0.01	0.05	0.09	0.41	0.49
(1.02, 0)	0.20	0.91	0.58	0.32	0.07
	0.10	0.11	0.06	3.23	2.32
	0.03	0.21	0.06	1.93	1.30
	0.01	0.16	0.02	2.25	1.51
Mean <sup>b</sup>		0.32	0.16	0.93	0.67

<sup>a</sup>Initial conditions are specified in Sec. II.<sup>b</sup>Average of 12 cases.

Shown in Table III is the average final value of the quantum-mechanical ground electronic-state probability density [i.e.,  $P_1(t=\infty)$  averaged over all the trajectories in the ensemble] for each of the 12 test cases and for both the FSTU and TFS methods. Also shown is the fraction of trajectories that finished the simulation in the ground electronic state [note that  $P_N \equiv F_1(t=\infty)$ ]. The FSTU method retains more self-consistency in the fewest-switches algorithm than the TFS method (i.e.,  $P_N$  is closer to  $\langle P_1(t=\infty) \rangle$  for the FSTU method). Also shown in Table III is the probability ( $f$ ) that a trajectory experienced a frustrated hop and finished the simulation in the ground electronic state. The FSTU method (by design) has less frustrated hopping than the TFS method by an average factor of 1.5.

The product of  $P_N$  and  $(1-f)$  (where  $1-f$  is the probability that a trajectory finished the simulation in the ground electronic state and did *not* experience a frustrated hop) is tabulated in Table III and gives a rough estimate of the fully

self-consistent fewest-switches result. These values agree very well with  $\langle P_1(t=\infty) \rangle$ , but do not agree with the accurate quantum-mechanical values of the total nonadiabatic quenching probability  $P_N^{\text{QM}}$ , also shown in Table III.

## V. DISCUSSION

The TFS method is formulated such that surface hops are minimized, and this “fewest-switches” formulation is accomplished by allowing surface hops only when there is a net flow of electronic state probability density out of the currently occupied electronic state during the interval between hopping decisions. The presence of classically forbidden electronic transitions destroys the self-consistency built into the TFS method, and results in a “fewer-than-fewest-switches” method. We note, however, that a fully self-consistent fewest-switches algorithm [i.e.,  $P_N \approx \langle P_1(t=\infty) \rangle$  in Table III] would greatly underestimate the accurate total

TABLE III. The quantum mechanical total nonadiabatic quenching probability  $P_N^{\text{QM}}$ , final ground electronic state probability density averaged over the ensemble of classical trajectories  $\langle P_1(t=\infty) \rangle$ , and the total nonadiabatic quenching probability  $P_N$  and frustrated hopping probability  $f$  for the TFS and FSTU methods.

I. C. <sup>a</sup>	$U_{12}^{\max}/\text{eV}$	$P_N^{\text{QM}}$ <sup>b</sup>	$\langle P_1(t=\infty) \rangle^c$	TFS			FSTU		
				$P_N$	$f$	$(1-f)P_N$	$P_N$	$f$	$(1-f)P_N$
(1.10, 0)	0.20	5.74(2) <sup>d</sup>	3.48(2)	9.87(2)	0.73	2.67(2)	7.51(2)	0.64	2.67(2)
	0.10	3.99(2)	1.80(2)	4.87(2)	0.65	1.72(2)	3.80(2)	0.55	1.72(2)
	0.03	4.10(3)	1.21(3)	5.71(3)	0.60	2.26(3)	4.44(3)	0.49	2.26(3)
	0.01	4.34(4)	2.79(4)	6.93(4)	0.59	2.87(4)	5.40(4)	0.47	2.87(4)
(1.10, 6)	0.20	1.62(1)	1.59(1)	1.97(1)	0.39	1.20(1)	1.73(1)	0.31	1.20(1)
	0.10	9.07(2)	1.11(1)	1.27(1)	0.29	9.05(2)	1.15(1)	0.21	9.05(2)
	0.03	1.59(2)	1.32(2)	1.57(2)	0.28	1.14(2)	1.42(2)	0.20	1.14(2)
	0.01	1.83(3)	1.48(3)	1.87(3)	0.27	1.37(3)	1.66(3)	0.18	1.37(3)
(1.02, 0)	0.20	4.97(2)	5.08(2)	9.66(2)	0.64	3.51(2)	7.84(2)	0.55	3.51(2)
	0.10	3.44(2)	1.99(2)	3.98(2)	0.60	1.61(2)	3.24(2)	0.50	1.61(2)
	0.03	3.71(3)	2.93(3)	4.21(3)	0.56	1.86(3)	3.49(3)	0.47	1.86(3)
	0.01	4.21(4)	2.79(4)	5.04(4)	0.55	2.26(4)	4.14(4)	0.45	2.26(4)

<sup>a</sup>Initial conditions are specified in Sec. II.<sup>b</sup>Accurate quantum-mechanical  $P_N$ ; these values are taken from Ref. 23.<sup>c</sup>Average value of the ground-state electronic probability density, averaged over all trajectories in the ensemble. This value is found to be the same for the TFS and FSTU methods for the number of figures presented.<sup>d</sup>Note that 5.74(2)  $\equiv 5.74 \times 10^{-2}$ .

nonadiabatic quenching probability  $P_N^{\text{QM}}$ . The fact that  $P_N^{\text{QM}} \neq \langle P_1(t=\infty) \rangle$  points out the serious problem in the semiclassical trajectory formalism that was mentioned earlier. Namely, the electronic state population density  $P_i(t)$  given by Eq. (1) does not properly include electronic state decoherence effects. A proper treatment of decoherence within the semiclassical trajectory approach would require that the electronic state density coherence  $a_{ij}$  depend on all of the trajectories in the ensemble, and thus would require simultaneous propagation of the entire ensemble of trajectories.<sup>22,52</sup> This would increase the computational complexity and cost of the surface-hopping algorithm, and we therefore restrict our attention to the independent trajectory approach.

One effect of the lack of proper treatment of the electronic state decoherence in the semiclassical trajectory approach is that the electronic state coherence term  $a_{ij}$  computed for each independent trajectory does not properly go to zero when the ensembles of trajectories in the two electronic states  $i$  and  $j$  separate in phase space. If for some fully decoherent trajectory  $a_{ij}$  is nonzero, there will be a flow of electronic state density (hopping) between electronic states, whereas an accurate treatment of  $a_{ij}$  would give  $a_{ij}=0$  and would damp out these (often frustrated) electronic transitions, as can be seen from Eqs. (1) and (2). The improper treatment of decoherence can have serious effects anywhere along the classical trajectory, but we note that a dramatic example of this problem occurs when the unoccupied electronic state is too high in energy to be occupied by any classical trajectories. When this is the case, there will be no trajectories directly “above” the ensemble of ground-state trajectories, and  $a_{ij}$  should therefore be nearly zero. As mentioned above, the independent semiclassical trajectory value of  $a_{ij}$  may not be zero, and a trajectory on the lower potential energy surface may therefore experience a frustrated hop in this region where a proper treatment of the decoherence would have predicted no hops at all.

From these considerations alone, one may be motivated to ignore all frustrated hopping as being caused by the lack of the proper treatment of the decoherence of divergent trajectories. We have shown, however, that ignoring all frustrated hopping (as in the TFS method) leads to systematic errors in the total nonadiabatic quenching probability.<sup>23</sup> The FSTU method, by allowing some frustrated hopping attempts to become successful nonlocal hops, greatly reduces these errors, as shown in Sec. IV. The FSTU method may be justified by noting that a quantum-mechanical nuclear wave function will have tails that extend into regions that are inaccessible to classical trajectories. These tails lead to electronic state population transfer in classically forbidden regions and therefore may induce frustrated hopping in the TFS algorithm, whereas this kind of hop is allowed by the FSTU method by incorporating nonlocal hopping into the fewest-switches formalism. The maximum “nonlocality” of a hop in the FSTU method corresponds to the approximate extension of the quantum-mechanical tails into the classically forbidden regions as estimated by Eq. (4).

Ideally, one would develop a method that incorporates the proper treatment of decoherence into the independent

semiclassical trajectory scheme by modifying the equations for calculating  $a_{ij}$  along the classical trajectory. Such a scheme, however, would still feature classically frustrated hopping as a result of the electronic state tunneling discussed above. The FSTU is a desirable practical alternative to an explicit treatment of decoherence effects because it is a simple extension of the TFS method. Its usefulness is further justified numerically in the present study, as it is shown to greatly improve the accuracy of the fewest-switches method.

The present formulation of the FSTU method is simple and straightforward, but it is not unique. For example, the uncertainty relation in Eq. (3) is strictly an inequality, and we can therefore write the FSTU nonlocal hopping criterion in Eq. (4) as

$$|t_0 - t_h| \leq x\hbar/2\Delta E, \quad (5)$$

where  $x$  is some number greater than or equal to 1. It is natural to take  $x=1$  (as in the FSTU method), but we also tested several variants of the FSTU method with different values of  $x$ , namely  $x=2, 4, 10$ , and  $\infty$  (where  $x=0$  is, of course, the TFS method). We found that the value of  $x=1$  gives the best agreement with the accurate quantum-mechanical results.

For some systems, it may be necessary to devise more complicated schemes for introducing nonlocal hopping into the fewest-switches algorithm such as alternate definitions of  $\Delta E$  or allowing trajectories to tunnel in some direction other than along the classical trajectory (say, along the nonadiabatic coupling vector). The FSTU method performs well without greatly increasing the complexity of the surface-hopping algorithm, and we did not test the more complicated schemes mentioned above. We did consider allowing trajectories to hop at any time (not just the closest time to  $t_0$ ) that satisfies the FSTU nonlocal hopping criteria in Sec. III by choosing between each time that satisfies these criteria with some probability. We found, however, that this modification had no significant effect on the values of the observables, and we can explain this by noting that the average value of  $\hbar/2\Delta E$  is much less than the characteristic time scales of the system. Therefore, resolving the hopping time within the  $\hbar/2\Delta E$  interval has little effect on the overall dynamics.

It is interesting to note that the problem of frustrated hopping has been addressed recently<sup>43,44</sup> using nonlocal hopping within the Landau–Zener trajectory surface-hopping scheme. The Landau–Zener trajectory surface-hopping scheme allows electronic transitions whenever a classical trajectory crosses some predefined hopping seam, and the hopping probability is computed from the electronic-state energies at the seam and the component of the nuclear momentum perpendicular to the hopping seam. Zhu *et al.* have proposed an elegant method<sup>43,44</sup> (which we will call the ZNN method) that incorporates nonlocal hopping into the Landau–Zener surface-hopping formalism. Specifically, frustrated hops are removed by allowing trajectories to tunnel perpendicular to the hopping seam. The ZNN method was shown to greatly improve the semiclassical trajectory results for the cases to which it was applied.

We note that the ZNN method differs from the FSTU method in several important ways. First, a FSTU trajectory,

like a TFS trajectory, may experience a hopping attempt anywhere along the classical trajectory and not only at a pre-defined hopping seam. We consider this to be essential for modeling many kinds of nonadiabatic systems, and hence we are only interested in the further development of methods with this generality. Second, the FSTU hopping probabilities are determined by integrating the time-dependent Schrödinger equation along the classical trajectory, whereas the ZNN hopping probabilities are based on information at the hopping seam. The ZNN hopping probabilities therefore do not suffer from the decoherence problem discussed here for the TFS method, at least when the assumptions underlying the Landau–Zener-type treatment are satisfied. Third, FSTU trajectories tunnel along the classical trajectory *in time* for some time that is no greater than that allowed by the uncertainty principle, whereas the ZNN trajectories tunnel *in space* perpendicular to the hopping seam and are not limited in their tunneling distance.

Other methods that delocalize the intersurface transitions are the full multiple spawning method,<sup>22,29</sup> which is based on the semiclassical propagation of Gaussian wave packets,<sup>53,54</sup> and methods based on a self-consistent or mean-field potential,<sup>11,14,16,19–21,25,28</sup> such as the semiclassical Ehrenfest method,<sup>11,14,16,25,28</sup> continuous surface switching,<sup>11,19,20</sup> and natural decay of mixing.<sup>21</sup> Our view is that there are three kinds of semiclassical molecular dynamics methods for non-Born–Oppenheimer systems, namely, trajectory surface-hopping methods, self-consistent potential methods, and wave packet propagation methods, and it is useful to find the best general method in each category as well as to compare different kinds of methods. We have previously presented arguments that the natural decay of mixing<sup>21</sup> is the best method of the self-consistent potential type, and the present paper indicates that the FSTU method appears to be a culmination of our efforts to find a best general method of the trajectory surface-hopping type. The systematic testing of standardized semiclassical wave packet methods is more in its infancy, but the FMS-M method has been proposed as a standardized validated method.<sup>22</sup> Comparing the methods between categories, we can summarize our previous studies<sup>11,14–16,18–23</sup> without repeating all the details by saying that the natural decay of mixing algorithm has the strong advantages that it avoids discontinuities (hops) and is independent of choosing an adiabatic or diabatic representation in strong interaction regions, whereas surface-hopping methods have an important advantage of simplicity of computer coding, and the Calaveras County criterion<sup>11,20–22</sup> provides a general prescription for choosing a representation. Both of these kinds of methods have the advantage over wave packet propagation methods that they are less expensive (at least with currently available computer programs<sup>45,55</sup>), and hence they facilitate a more thorough sampling of the space of the initial conditions, making realistic simulations more feasible.

It has been noted above that the FSTU method has more surface switches than the TFS method. This should not be seen as a violation of the fewest-switches formulation. As discussed above, the presence of frustrated hops in the TFS method results in a fewer-than-fewest-switches method. Only in the limit of a fully self-consistent surface-hopping

method does the number of hops *increase* such that the method becomes the fewest-switches method as it was originally formulated. The FSTU method is, in fact, closer than the TFS method to the fewest-switches fully self-consistent result.

## VI. CONCLUSIONS

We have described a new method for treating classically forbidden electronic transitions in trajectory surface-hopping calculations; the new method is called the fewest-switches with time uncertainty (FSTU) algorithm. The FSTU method improves the self-consistency of the fewest-switches algorithm. We tested the FSTU method using a set of 12 three-body, two-state test cases that were designed to provide sensitive tests of methods for treating weakly coupled highly quantal systems, and hence provide a challenging test of methods for correcting the problem of frustrated hopping. We found that the new formalism greatly increases the accuracy of the total nonadiabatic quenching probability and the product branching ratio.

## ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation under Grant No. CHE00-92019.

- <sup>1</sup>J. C. Tully, in *Dynamics of Molecular Collisions*, edited by W. H. Miller (Plenum, New York, 1976), Part B, pp. 217–267.
- <sup>2</sup>D. G. Truhlar and J. T. Muckerman, in *Atom–Molecule Collision Theory*, edited by R. B. Bernstein (Plenum, New York, 1979), pp. 505–566.
- <sup>3</sup>H. Nakamura, *Adv. Chem. Phys.* **82**, 243 (1992).
- <sup>4</sup>E. A. Gislason, G. Parlant, and M. Sizun, *Adv. Chem. Phys.* **82**, 321 (1992).
- <sup>5</sup>S. Chapman, *Adv. Chem. Phys.* **82**, 423 (1992).
- <sup>6</sup>M. F. Herman, *Annu. Rev. Phys. Chem.* **45**, 83 (1994).
- <sup>7</sup>H. Nakamura, in *Dynamics of Molecules and Chemical Reactions*, edited by R. E. Wyatt and J. Z. H. Zhang (Dekker, New York, 1996), pp. 473–529.
- <sup>8</sup>J. C. Tully, in *Modern Methods for Multidimensional Dynamics Computations in Chemistry*, edited by D. C. Thompson (World Scientific, Singapore, 1998), pp. 34–72.
- <sup>9</sup>J. C. Tully, *Faraday Discuss. Chem. Soc.* **110**, 407 (1998).
- <sup>10</sup>E. E. Nikitin, *Annu. Rev. Phys. Chem.* **50**, 1 (1999).
- <sup>11</sup>M. D. Hack and D. G. Truhlar, *J. Phys. Chem. A* **104**, 7917 (2000).
- <sup>12</sup>M. S. Topaler, M. D. Hack, T. C. Allison, Y.-P. Liu, S. L. Mielke, D. W. Schwenke, and D. G. Truhlar, *J. Chem. Phys.* **106**, 8699 (1997).
- <sup>13</sup>M. S. Topaler, T. C. Allison, D. W. Schwenke, and D. G. Truhlar, *J. Phys. Chem. A* **102**, 1666 (1998).
- <sup>14</sup>M. S. Topaler, T. C. Allison, D. W. Schwenke, and D. G. Truhlar, *J. Chem. Phys.* **109**, 3321 (1998); **110**, 687(E) (1999); **113**, 3928(E) (2000).
- <sup>15</sup>Y. Zeiri, G. Katz, R. Kosloff, M. S. Topaler, D. G. Truhlar, and J. C. Polanyi, *Chem. Phys. Lett.* **300**, 523 (1999).
- <sup>16</sup>Y. L. Volobuev, M. D. Hack, and D. G. Truhlar, *J. Phys. Chem. A* **103**, 6225 (1999).
- <sup>17</sup>M. D. Hack, A. W. Jasper, Y. L. Volobuev, D. W. Schwenke, and D. G. Truhlar, *J. Phys. Chem. A* **103**, 6309 (1999).
- <sup>18</sup>M. D. Hack, A. W. Jasper, Y. L. Volobuev, D. W. Schwenke, and D. G. Truhlar, *J. Phys. Chem. A* **104**, 217 (2000).
- <sup>19</sup>Y. L. Volobuev, M. D. Hack, M. S. Topaler, and D. G. Truhlar, *J. Chem. Phys.* **112**, 9716 (2000).
- <sup>20</sup>M. D. Hack and D. G. Truhlar, *J. Chem. Phys.* **114**, 2894 (2001).
- <sup>21</sup>M. D. Hack and D. G. Truhlar, *J. Chem. Phys.* **114**, 9305 (2001).
- <sup>22</sup>M. D. Hack, A. M. Wensmann, D. G. Truhlar, M. Ben-Nun, and T. J. Martinez, *J. Chem. Phys.* **115**, 1172 (2001).
- <sup>23</sup>A. W. Jasper, M. D. Hack, and D. G. Truhlar, *J. Chem. Phys.* **115**, 1804 (2001).
- <sup>24</sup>S. L. Mielke, G. J. Tawa, D. G. Truhlar, and D. W. Schwenke, *Chem. Phys. Lett.* **234**, 57 (1995).



- <sup>25</sup>H.-D. Meyer and W. H. Miller, J. Chem. Phys. **70**, 3214 (1979).
- <sup>26</sup>N. C. Blais and D. G. Truhlar, J. Chem. Phys. **79**, 1334 (1983).
- <sup>27</sup>J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).
- <sup>28</sup>A. García-Vela, R. B. Gerber, and D. G. Imre, J. Chem. Phys. **97**, 7242 (1992).
- <sup>29</sup>T. J. Martinez, M. Ben-Nun, and R. D. Levine, J. Phys. Chem. **100**, 7884 (1996); **101**, 6839 (1997).
- <sup>30</sup>U. Müller and G. Stock, J. Chem. Phys. **107**, 6230 (1997).
- <sup>31</sup>J.-Y. Fang and S. Hammes-Schiffer, J. Phys. Chem. A **103**, 9399 (1999).
- <sup>32</sup>J. C. Tully, Int. J. Quantum Chem., Symp. **25**, 299 (1991).
- <sup>33</sup>A. Bjerre and E. E. Nikitin, Chem. Phys. Lett. **1**, 179 (1967).
- <sup>34</sup>R. K. Preston and J. C. Tully, J. Chem. Phys. **54**, 4297 (1971); J. C. Tully and R. K. Preston, *ibid.* **55**, 562 (1971).
- <sup>35</sup>W. H. Miller and T. F. George, J. Chem. Phys. **56**, 5637 (1972).
- <sup>36</sup>P. J. Kuntz, J. Kendrick, and W. N. Whitton, Chem. Phys. **38**, 147 (1979).
- <sup>37</sup>M. F. Herman, J. Chem. Phys. **81**, 754 (1984).
- <sup>38</sup>N. C. Blais, D. G. Truhlar, and C. A. Mead, J. Chem. Phys. **89**, 6204 (1988).
- <sup>39</sup>G. Parlant and E. A. Gislason, J. Chem. Phys. **91**, 4416 (1989).
- <sup>40</sup>P. J. Kuntz, J. Chem. Phys. **95**, 141 (1991).
- <sup>41</sup>J.-Y. Fang and S. Hammes-Schiffer, J. Chem. Phys. **110**, 11166 (1999).
- <sup>42</sup>See endnote 39 in S. Hammes-Schiffer and J. C. Tully, J. Chem. Phys. **101**, 4657 (1994).
- <sup>43</sup>C. Zhu, K. Nobusada, and H. Nakamura, J. Chem. Phys. **115**, 3031 (2001).
- <sup>44</sup>C. Zhu, H. Kamisaka, and H. Nakamura, J. Chem. Phys. **115**, 11036 (2001).
- <sup>45</sup>E. Neria, A. Nitzan, R. N. Barnett, and U. Landman, Phys. Rev. Lett. **67**, 1011 (1991); O. V. Prezhdo and P. J. Rossky, J. Chem. Phys. **107**, 5863 (1997).
- <sup>46</sup>A. W. Jasper, Y. L. Volobuev, M. S. Topaler, T. C. Allison, M. D. Hack, Y.-P. Liu, S. N. Stechmann, T. F. Miller, III, N. C. Blais, and D. G. Truhlar, NAT—version 6.6 (University of Minnesota, Minneapolis, 2000).
- <sup>47</sup>D. F. Coker and L. Xiao, J. Chem. Phys. **102**, 496 (1995).
- <sup>48</sup>J. J. Sakurai, *Modern Quantum Mechanics* (Addison-Wesley, Redwood City, CA, 1985), pp. 78–80.
- <sup>49</sup>D. G. Truhlar, B. P. Reid, D. E. Zurawski, and J. C. Gray, J. Phys. Chem. **85**, 786 (1981).
- <sup>50</sup>M. S. Topaler and D. G. Truhlar, J. Chem. Phys. **107**, 392 (1997).
- <sup>51</sup>W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in FORTRAN*, 2nd ed. (Cambridge University Press, Cambridge, UK, 1994), pp. 716–725.
- <sup>52</sup>R. B. Gerber, V. Buch, and M. A. Ratner, J. Chem. Phys. **77**, 3022 (1982); C. C. Martens and J.-Y. Fang, *ibid.* **106**, 4918 (1997); S. Neilsen, R. Kapral, and G. Cicotti, *ibid.* **112**, 6543 (2000); A. Donoso, D. Kohen, and C. C. Martens, *ibid.* **112**, 7345 (2000).
- <sup>53</sup>E. J. Heller, J. Chem. Phys. **75**, 2923 (1981).
- <sup>54</sup>R. T. Skodje and D. G. Truhlar, J. Chem. Phys. **80**, 3123 (1984).
- <sup>55</sup>M. D. Hack, D. G. Truhlar, M. Ben-Nun, T. J. Martinez, and R. D. Levine, FMS90—version 2.1 (University of Minnesota, Minneapolis, and University of Illinois, Urbana, 2000).